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A narrow line UV-induced non-persistent radical in view of generating highly polarized transportable glucose solid samples

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Dynamic nuclear polarization (DNP) is a versatile technique for polarizing nuclear spins through polarization transfer from unpaired electron spins by microwave irradiation at the appropriate frequency.¹ The unpaired electron spins are usually introduced in the form of persistent radicals dissolved in a liquid sample containing the molecules bearing the nuclear spins, target of the polarization transfer. DNP can yield the highest polarizations at low temperature (1–4 K), once the sample is in the solid state, and at moderate magnetic field (3.35–7 T). It was shown that the high nuclear polarizations obtained after solid-state DNP can be maintained in the liquid-state if the frozen sample is rapidly dissolved inside the polarizer.²

The main limitation of dissolution DNP concerns the need to place the polarizer as close as possible to the MRI scanner (or high resolution spectrometer) where the actual hyperpolarized (HP) magnetic resonance experiment is performed. Indeed, after dissolution the life-time of the HP liquid is limited by spin-lattice relaxation that brings the nuclear spin populations back to thermal equilibrium, generally in less than a minute.

It was recently demonstrated that photo-induced radicals, generated via UV-light irradiation of frozen solutions containing a fraction of pyruvic acid (PA), are suitable to perform DNP on several substrates.³ The unique property of this polarizing agent is represented by their non-persistence: they suffer from thermal stress and they are naturally scavenged if the temperature of the DNP sample is raised above 190 K. Thus, they can be eliminated while the sample is still frozen inside the polarizer through a fast thermalization process, yielding radical-free highly polarized solid samples.⁴ The latter, because of the absence of paramagnetic species, can be extracted from the polarizer, stored in appropriate conditions of temperature and magnetic field, transported and dissolved with negligible polarization loss at another location and time.^{4,5}

In the present work, we tackled the main drawback associated to the photo-induced non-persistent radicals: the relatively low ¹³C polarization (up to 13% at 7 T and 1 K),⁴ when compared to trityl radicals.⁶ This is due to the larger ESR line width of the radical when PA is the precursor. A precursor with more narrow ESR line was studied on ¹³C-glucose, a substrate showing increasing interest among the dissolution DNP community.⁷

Two samples were prepared to test the DNP properties of the new UV-induced non-persistent radical precursor, i.e. trimethyl pyruvic acid (Tri-PA). 3 M of [U-²H, U-¹³C] were dissolved in a mixture of PA:H₂O 1:1 (v/v) (7 M of radical precursor) and in one of Tri-PA:H₂O:Ethylene glycol 2:4:4 (v/v/v) (1.6 M of radical precursor). The first sample was used as reference. For each sample 60 frozen pellets were made pouring 4.0±0.5 µL droplets of solution into a transparent quartz dewar (Wilma-LabGlass WG-850-B-Q) filled with liquid nitrogen. The samples were irradiated for 120 s with a high power (20 W/cm²) broadband UV source (Dymax BlueWave 75). X-band ESR measurements (Magnetech MiniScope 5000) showed, for both samples, a radical concentration of 30±5 mM (see Fig 1). Each sample was then transferred to a 6.7 T/1.1 K polarizer. DNP microwave sweeps are shown in Fig 2. For both samples modulation of the microwave frequency (25 MHz amplitude at 1 kHz) allowed doubling the maximum solid-state DNP enhancement. After about 90 min, a ¹³C polarization of 27±3 % (time constant 1900±50 s) or 50±5 % (time constant 2000±100 s) was measured for the samples containing as radical precursor PA and Tri-PA, respectively. Trityl under the same conditions would achieve 70% polarization.⁶ The higher polarization achieved using the new molecule is in good agreement with its sharper ESR spectrum. Since the unpaired electron is localized on the beta carbon of the molecules, “pushing” the methyl groups further away reduces the hyperfine coupling between the electron and the molecule’s nuclear environment, providing a DNP radical with features closer to trityl.

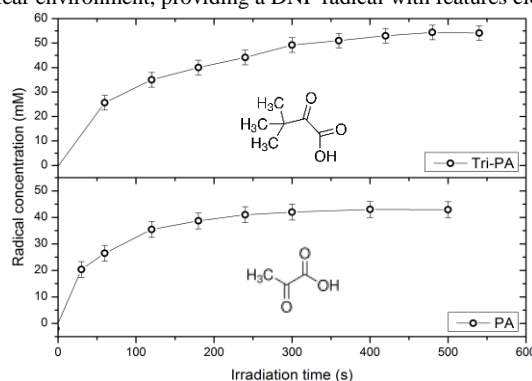


Figure 1 Radical generation as a function of the irradiation time for the sample containing Tri-PA as precursor (top) and PA as precursor (bottom).

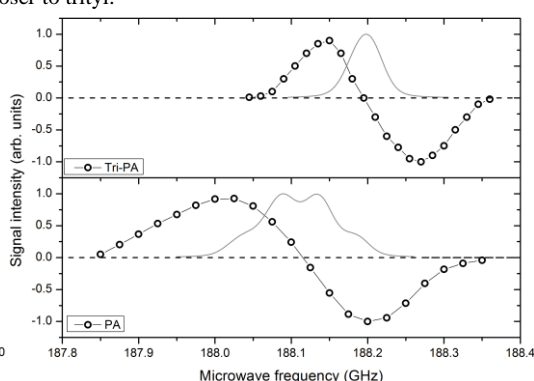


Figure 2 ¹³C DNP microwave sweep at 1 K and 6.7 T for the sample containing Tri-PA as precursor (top) and PA as precursor (bottom).

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